EFFECT OF ZEOLITE CONCENTRATION ON DEVELOPMENT OF POLYETHERSULFONE MIXED MATRIX MEMBRANES (MMMs) FOR O_2/N_2 SEPARATION

MUHAMMAD HIDAYAT BIN MUSA

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Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

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ABSTRACT

The membrane gas separation is an effective economical process to separate gas such as oxygen (O_2) and nitrogen (N_2) gases. The limited selectivity and permeability trade off of plain polymeric membrane have force researchers in finding alternatives to improve polymeric membrane performance. With the insertion of inorganic filler in polymer solution such as zeolite , mixed matrix membranes (MMMs) was produced. In this study, the effect of concentration zeolite loading was studied in order to identify optimum composition for the best separation performance. The polymer solution contains Polyethersulfone (PES) as the polymer, N-Methyl Pyrrolidone (NMP) as the solvent and distilled water (H_2O) as the non-solvent. The zeolite concentration valued between 5 to 20 wt % was applied. To increase the compatibility of zeolite with the polymer, 3-Aminopropyl-Trimethoxysilane (APTMOS) was used to treat the zeolite prior to dope formulation to modify the zeolite surface. The dry/wet phase inversion method was used to produce the asymmetric flat sheet membrane. The prepared membrane was coated with silicone and N-Hexane to decrease the surface defect of the membrane. In order to determine the membrane performance, the membranes were tested using O_2 and N_2 as the test gases using permeability test rig. The surface and cross section image of the prepared membrane was identified by using Scanning Electron Microscope (SEM). The results show that the MMMs with 15 % concentration of zeolite possessed the highest selectivity of 3.3 while the lowest selectivity is at 5 % zeolite concentration that is 1.3 and the optimum pressure was found at 3 bar. Therefore it proves that by insertion of zeolite at 15 wt% provides an interconnected channel that will only allow the flow of O_2 and preventing N_2. As a conclusion by increasing concentration of zeolite loading, the high selectivity and high permeability of MMMs will be increased.

ABSTRAK

Proses pengasingan gas menggunakan membran adalah salah satu dari proses yang ekonomikal dan berhemat untuk mengasingkan gas oksigen (O_2) dan nitrogen (N_2).Kadar pemilihan dan resapan terhadap gas yang terhad oleh membran polimer telah mendesak para penyelidik untuk mencari alternatif untuk mempertingkatkan prestasi dan kemampuan polimer membran. Dengan penambahan bahan bukan organik di dalam larutan polimer contohnya seperti zeolit, membran campuran matrik (MMMs) akan terhasil. Dalam kajian ini, efek kepekatan zeolit yang ditambah dikaji untuk mendapatkan komposisi optimum terbaik. Larutan polimer terdiri daripada Poliethersulfona (PES) sebagai polimer, N-Metil Pyrrolidona (NMP) sebagai pelarut dan air suling (H_2O) sebagai bahan tambah bukan pelarut. Kepekatan zeolit yang dikaji adalah di antara 5 hingga 20 % jisim. Untuk meningkatkan keserasian antara zeolit dan polimer, 3-Aminopropil-Trimetoksisilan (APTMOS) digunakan untuk mengubahsuai permukaan zeolit sebelum penghasilan larutan polimer. Proses fasa balikan kering/basah digunakan untuk memghasilkan membran asimetrik kepingan rata. Membran yang terhasil akan disalut dengan silikon dan N-Heksana untuk tujuan mengurangkan kecacatan pada permukaan membran. Membran yang terhasil diuji mengunakan gas O_2 dan gas N_2 sebagai gas ujian pada mesin penguji kadar penembusan dan imej permukaan serta keratin rentas membran yang terhasil, didapati menggunakan Mikroskop Pengimbas Elektron (SEM). Keputusan kajian menunjukkan MMMs yang berkepekatan zeolit 15% mempunyai kadar pemilihan yang tertinggi iaitu, 3.3 manakala pemilihan yang paling rendah didapati pada kepekatan zeolit 5% iaitu 1.3 dan tekanan optimum adalah pada 3 bar .Oleh itu dapat dibuktikan bahawa penambahan zeolit sebanyak 15 % menjadikan ikatan zeolit dan zeolit yang mana akan hanya membenarkan pengaliran gas O_2 dan menghalang pengaliran gas N_2. Oleh yang demikian, dapat disimpulkan peningkatan kepekatan zeolit dalam membran, kedua-dua kadar penyerapan dan pemilihan MMMs pasti meningkat.

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Abbreviations

CO_2	-	Carbon Dioxide
H_2	-	Hydrogen
MMMs	-	Mixed Matrix Membranes
AlO_4	-	Aluminium Oxide
SiO_4	-	Silicone Oxide
O_2	-	Oxygen
N_2	-	Nitrogen
NH2	-	Amino Group
SEM	-	Scanning Electron Microscopic
GS	-	Gas Separation
H_2O	-	Water
PES	-	Polyethersulfone
NMP	-	1-methyl-2-pyrrolidone
APTMOS	-	3-Aminopropyl- Trimethoxysilane
UK	-	United Kingdom
GPU	-	Gas Permeation Unit
MW	-	Molecular Weight
Wt%	-	Weight percentage
°C	-	Degree celcius
V/V	-	Volume over volume total
STP	-	Standard Pressure and Temperature

Parameters/Symbols

P	-	Overall permeability
P_c	-	Permeability of the continuous polymer phase ($\frac{cm^3}{cmHg\ s\ cm^2}$)
P_d	-	Permeability of the dispersed zeolite phase ($\frac{cm^3}{cmHg\ s\ cm^2}$)
α	-	Selectivity (Unitless)
Q	-	Flow rate of gas species (cm^3/s)
A	-	Area of membrane (cm^2)
ΔP	-	Pressure difference across membrane (cm Hg)
M	-	Charge balancing cation
n	-	cation valence
w	-	Moles of water contained in the zeolitic voids
Å	-	Amstrong
µm	-	Micrometer
cm	-	Centimeter
%	-	Percentage
Kg	-	Kilogram
g	-	Gram
M_i	-	Molecular weight species i (g/mol)
$\boldsymbol{\eta_i}$	-	Viscosity species i (µPa s)
$\boldsymbol{\sigma_i}$	-	Collision diameter i (cm)
(P/*l*)	-	Pressure Normalized Flux (cm^3 (STP)/ cm^2. s. cmHg)

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Gas separation is one of the technologies that become wider and getting more attention each year. By applying gas separation we can obtain more pure products. The examples of gas separation processes are absorption, cryogenic distillation and gas permeation (Bernardo *et. al*, 2009). Gas separation process is applied in many processes in the chemical industry such as separation of acid gases like CO_2 from natural gas, separation of H_2 from CO_2 for the product of fermentation using carbohydrate rich substrate (Khan *et. al*, 2010).

Gas permeation process is a gas separation process that uses polymeric membrane and it is an attractive process because of its low energy consumption, simple operation and low maintenance requirements (Sen *et. al*, 2007; Khan *et. al*, 2010). The application of polymeric membranes is limited by the permeability and selectivity trade off (Robeson, 1991). Both membrane's permeability and selectivity influence the economics of a gas separation membrane process.

As stated before the polymeric membrane have a limitation on the trade-off between permeability and selectivity. As the selectivity increase, the permeability tends to decrease and vice versa (Bernardo *et. al*, 2009). Chain stiffness and interchain separation increases are recognized as ways to systematically improve separation performance until the interchain separation becomes large enough that the polymer segmental motion no longer controls penetrant diffusion. Other than that, polymeric membrane cannot withstand high temperature and aggressive chemical environments (Bernardo *et. al*, 2009).The development of inorganic membranes such as silica membranes, zeolites membrane and carbon based molecular sieve was introduced because they can with stand aggressive chemicals as well as high temperatures. But these material also present drawbacks such as high cost, modest reproducibility, brittleness, low permeability in the case of highly selective dense membrane and difficult sealing at high temperature (Bernardo *et. al*, 2009).

The combination of the polymer membrane and inorganic membrane produce a new type of materials called Mixed Matrix Membranes (Bernardo *et. al*, 2009). Mixed Matrix Membranes (MMMs) have recently emerged as promising membrane morphology for gas separation. Their microstructure consists of an inorganic materials incorporated into a polymeric matrix by embedding a filler material into the polymer matrix (Bernardo *et. al*, 2009; Sen *et. al*, 2007). The examples of the fillers are carbon molecular sieve and zeolite molecular sieve. MMMs combine the easy processability of the polymer with the size sieving properties of the molecular sieving material (Khan *et. al*, 2010).

Zeolite is a mineral and they are crystalline alumino-silicates consisting AlO_4 and SiO_4 tetrahedral that are connected to form a network of channels and cavities (Khan *et. al*, 2010). The insertion of Zeolite in the polymeric membrane does increase the permeability and selectivity of the membrane towards the gases. The successful development of MMMs depends on several factors, such as the proper selection of polymer matrix and inorganic fillers and the elimination of interfacial defects between

the two phases. It is also important to control the filler concentration, shape and dimensions to obtained best results (Bernardo *et. al*, 2009).

A result of a research on gas permeation characteristics of polymer-zeolite mixed matrix membranes (the MMMs of the polyethersulfone and zeolite [4A and 13X]) by Suer, for mixed matrix membrane between PES and zeolite 13X, for zeolite loading rate between 0.0% to 8.3% the permeability of N_2 gas decreases from 0.14 to 0.077 barrer. For loading rate of zeolite from 16.6% to 50.0%, the permeability of N_2 gas increases from 0.088 to 0.12 barrer. While for the selectivity of O_2/ N_2 gas, with the increase of zeolite loading rate, from 0.0% to 50.0%, the selectivity increases from 3.71 to 4.18 (Suer *et. al*, 1994) .Therefore, by varying the zeolite concentration, it will expect to produce membrane with the best separation performance for gas separation.

1.2 Problem Statement

The concentration or the loading rate of the zeolite into the polymer matrix during membrane fabrication plays an important role on determining and production of the expected membrane that will allow maximum gas separation process. According to Sen and co-worker, the increasing zeolite loading rate will increase the membrane selectivity and the permeability of the membrane. But at high loading rate, the selectivity of the membrane will decrease and increase the permeability for certain membrane morphology (Mixed matrix membrane of polyethylene imene and silicate-1) (Sen *et. al*, 2007). While on the other hand, Suer and co-worker, reported that, at low zeolite loading rate, the permeability decrease, while the selectivity increase for the MMMs of the polyethersulfone and zeolite (Suer *et. al*, 1994). But at high zeolite loading rate both selectivity and permeability increases. This shows that the concentration of the zeolite must be at the optimum point to have the highest permeability and selectivity. Therefore this study will focus on the effect of zeolite

concentration on the development of polyethersulfone mixed matrix membranes for O_2 and N_2 gas separation

1.3 Objective

Based on the problem statement described in the previous section, the following are the objectives of this research:

1. To develop MMMs for O_2/ N_2 gas separation by varying the composition of zeolite during dope formulation.
2. Correlating membrane performance with fabrication conditions hence producing MMMs for O_2/ N_2 gas separation.
3. To study membrane morphology.
4. To identified the optimum zeolite loading by analyzing the membrane performance.

1.4 Scope of Study

In order to achieve the above mentioned objective the following scopes were drawn:

1. Characterization of coated and uncoated membrane using pure N_2 and O_2 as test gas.
2. Morphological studies of the surface layer and cross section of the developed membrane using Scanning Electron Microscopy (SEM).
3. Varying the percentage of zeolite loading in dope formulation.

1.5 Benefit and Significant of Research

By doing a research on the development of mixed matrix membrane, with the insertion a certain concentration of zeolite in the matrix of the polymeric membrane, possibly the permeability and selectivity will increase, therefore we will get a better separation of gas and it leads to more cost and energy saved. More pure product will be obtained, so the product receive by the consumer will be at a satisfactory level and if there is a downstream process waits, this will ensure a better result for downstream processes that use the product.

CHAPTER 2

LITERATURE REVIEW

3.1 Historical Development of Membranes

Studies of membrane can be traced back to the eighteenth century. A good example is Abbé Nolet started the use of the word Osmosis for the description of permeation of water from a lower concentration to a higher concentration through a diaphragm in 1748. For next two centuries the application of membrane are still limited with no commercial used but still it was used as a laboratory tools in developing physical and chemical theories (Baker, 2000). Table 2.1 show the overall events on the membrane technology development 1960s to 1980s.

Table 2.1: Historical background and the development of membrane technology (Baker, 2000)

Year/ century	Researcher/ scientist	Events
1748	Abbé Nolet	Introduced the word osmosis for water permeation through diaphragm
1867	Moritz Traube and W.Pfeffer	Introduced a fortified copper-ferrocyanide membrane that allows water to move from diluted to the concentrated parts.
1887	Van't Hoff	Introduction of Van't Hoff equation that explain the behaviour of ideal dilute solutions
1907	Bechhold	Devised a technique called dry phase inversion method to prepare nitrocellulose (collodion) membranes
1918	Zsigmondy and Bachmann	Improve Bechhold method and patent the dry phase inversion method
1930s	-	Microporous collodion membranes were commercially available.
1940s	US army	Develop filters to test water safety for drinking at the end of World War II
1945	W.J.Kolf	Demostrated the first successful artificial kidney based on membrane separation concept
1947	Goetz	Produce cellulose acetate-cellulose nitrate microfiltration membrane by vapor induced phase inversion
1954	Milipore corp.	Commercialized Goetz'smembrane
1960s	Sidney Loeb and S. Sourirajan	Development and introduction of their method of making defect-free, high flux, anistropic reverse osmosis membrane
1966	Alex Zaffaroni	Founder of membranes for controlled drug delivery systems
1980s	-	-First major development of membrane application in industry -Mansato Prism membrane produce for hydrogen separation
1980s	GFT(Germany engineering company)	Introduction of the first commercial pervaporation systems for dehydration of alcohol

In the 1980s separation by using membranes, emerged as a commercial process on a large scale. In this period, significant progress was made in virtually every aspect of membrane technology, including improvements in membrane formation processes (including interfacial polymerization and multiplayer composite casting and coating), chemical and physical structures, configuration and applications.

2.2 Membrane Separation Technology

Membrane can be defined as a thin barrier between the two bulk phases and it is either a homogeneous phase or a heterogeneous collection of phases (Pandey and Chauhan, 2001). The membrane is a permselective barrier that permits transport of some component but retains others. The flow of material across a membrane is kinetically driven by the application of pressure concentration, vapour pressure, hydrostatic pressure, electrical potential, or temperature (Norida, 2004). According to Baker, the category, process and the status of types of membrane technology can be seen in Table 2.2.

Table 2.2: Membrane Processes (Baker, 2000)

Category	**Process**	**Status**
Developed industrial membrane separation technology	Microfiltration Ultrafiltration Reverse Osmosis Electrodialysis	Well establish unit operation. No major breakthrough seem imminent
Developing industrial membrane separation technologies	Gas separation Pervaporation	A number of plants have been installed. Market size and number of applications served are expanding
To-be-developed industrial membrane separation technology	Carrier facilitated transport Membrane contractors Piezodialysis	Major problems remain to be solved before industrial systems will be installed on large scale
Medical application of membrane	Artificial Kidneys Artificial Lungs Controlled drug deliveries	Well establish processes. Still the focus of research to improve performance, for example, improving biocompatibility

The four developed industrial application of membrane separation processes are microfiltration, ultrafiltration, reverse osmosis, and electrodialysis. Figure 2.1 showing the range of application for reverse osmosis, ultrafiltration, microfiltration, pervaporation and gas separation according to their gas transport mechanism and also based on their pore size (Baker, 2000).

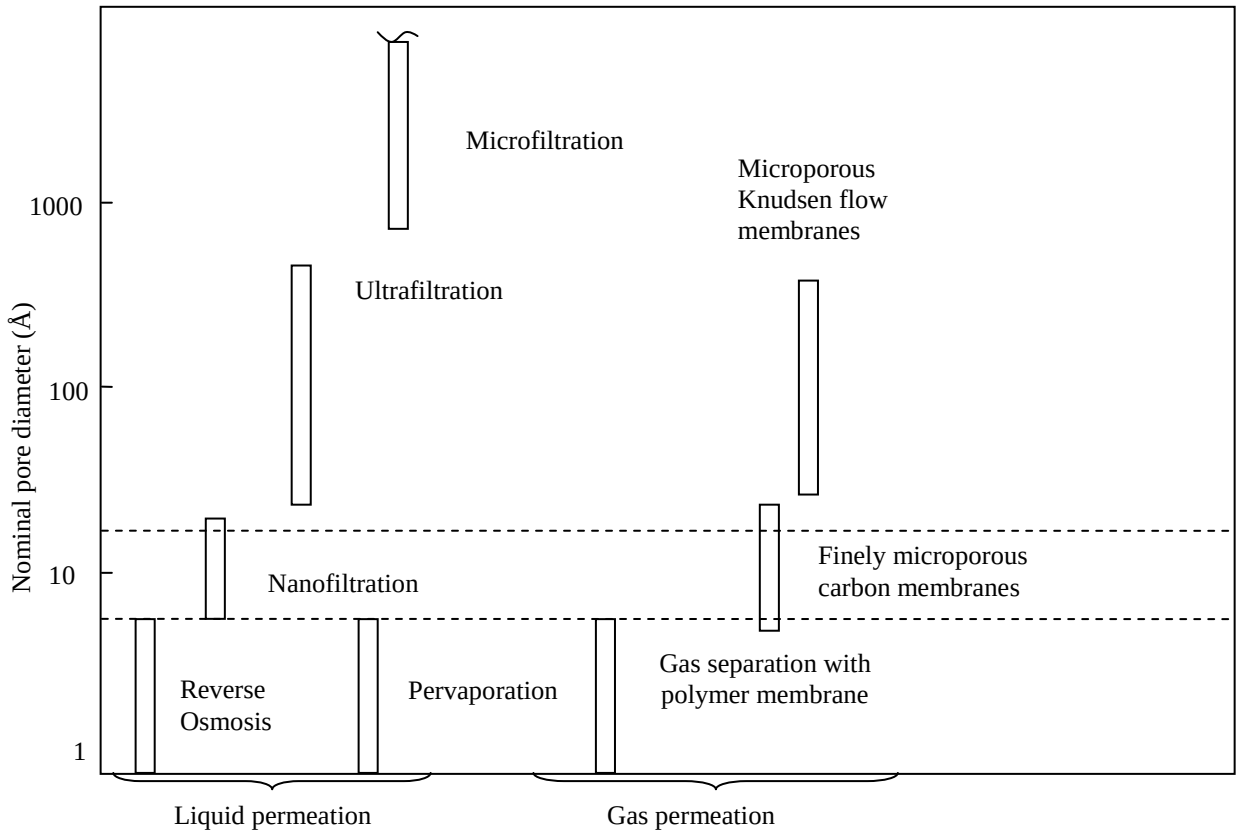

Figure 2.1: Schematic representation of nominal pore size for the principal membrane separation processes (Baker, 2000)

Reverse osmosis, ultrafiltration, microfiltration and conventional filtration are related processes differing principally in the average pore diameter of the membrane filter. Microfiltration membranes filter colloidal particles and bacteria from 0.1 to 10 μm in diameter. Ultrafiltration membranes can used to filter dissolve macromolecules such as proteins, from solutions. The mechanism of separation by reverse osmosis is quite different. Reverse osmosis membranes are so dense that discrete pores are so small, from 3 to 5 Å in diameter that they are within the range of thermal motion of the polymer chains that form the membrane does not exist and therefore the transport

occurs via statistically distributed free volume areas. This mechanism is called solution-diffusion (Baker, 2000).

The fourth fully developed membrane process is electrodialysis in which charged membranes are used to separate ions from aqueous solutions under the driving force of an electrical potential difference. The process utilizes the electrodialysis stack, built on the filter-press principle and containing several hundred individual cells, each formed by pairs of anion and cation exchange membranes. The principal application of electrodialysis is the desalting of brackish groundwater (Baker, 2000).

There are two developing membrane application, gas separation and pervaporation. In gas separation, a gas mixture at an elevated pressure is passed across a surface of membrane that is selectively permeable to one component of the feed mixture and the membrane permeates will enriched with that species (Baker, 2000). Pervaporation is relatively new process that has element in common with reverse osmosis and gas separation. In pervaporation, a liquid mixture contacts on membrane at one side, and the permeates escape on the other side as vapour. The main industrial application of pervaporation is the dehydration of ethanol solutions (Baker, 2000).

2.3 Mixed Matrix Membrane

Mixed-matrix membranes (MMMs) microstructure consists of an inorganic material incorporated into a polymeric matrix. The use of two materials with different flux and selectivity provides the possibility to better design a Gas Separation (GS) membrane, allowing the synergistic combination of polymers' easy processability and the superior GS performance of inorganic materials (Bernardo *et. al*, 2009)

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In principle, the incorporation of the inorganic component can be seen as a relatively easy modification of existing methods for fabricating large-surface area polymeric membranes; therefore, MMMs possess an economic advantage over inorganic membranes. In addition, they may offer enhanced physical, thermal, and

mechanical properties for aggressive environments and could be a way to stabilize the polymer membrane against change in permselectivity with temperature (Hu *et. al*, 1997).

The performance of various membrane materials available for the separation of O_2/N_2 is depicted in Figure 2.2.

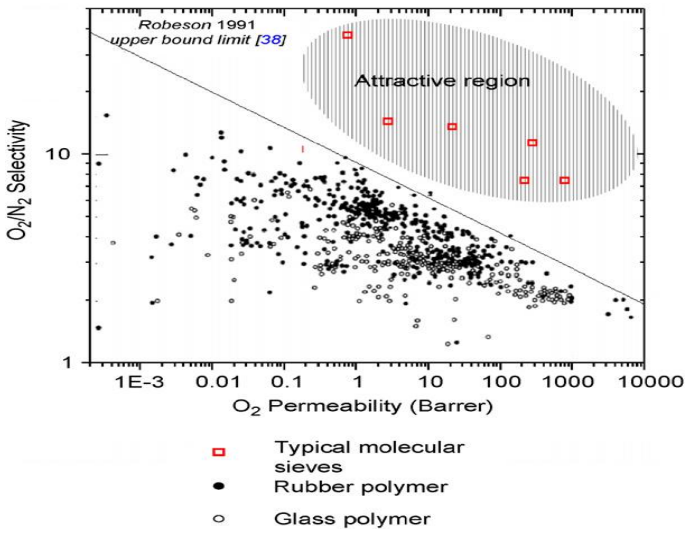

Figure 2.2: Relationship between the O_2/N_2 selectivity and O_2 permeability for polymeric membranes and inorganic membranes (Robeson, 1991)

From Figure 2.2, the selectivity and permeability limit has become an obstacle for polymeric membrane to exceed beyond the upper bound limit. On the other hand, inorganic membranes was way far beyond the upper limit bound showing it have high selectivity and permeability. However, inorganic membranes is still seriously hindered by the lack of technology to form continuous and defect-free membranes, the extremely high cost for the membrane production, and handling issues (Saracco *et.al*, 1999). The latest membrane morphology emerging involves MMMs, consisting of organic polymer and inorganic particle phases.

At relatively low loadings of zeolite particles, permeation occurs by combination of diffusion through the polymer phase and diffusion through the permeable zeolite particles. The relative permeation rates through two phases are determined by their

permeability. At low loadings of zeolite, the effect of the permeable zeolite particle on permeation can be expressed mathematically by the expression shown in equation 2.1, developed first by Maxwell in 1970s (Baker, 2000; Nunes and Peinemann, 2001; Chung *et. al*, 2007).

$$P = P_C[\frac{P_d+2P_c-2\Phi(P_c-P_d)}{P_d+2P_c+\Phi(P_c-P_d)}] \qquad (2.1)$$

Where P is the overall permeability of the mixed matrix material, Φ is the volume fraction of the dispersed zeolite phase, P_c is the permeability of the continuous polymer phase and P_d is the permeability of the dispersed zeolite phase. If this equation is used to calculate the permeability of the mixed matrix membrane, the equation to be used to calculate the selectivity is as equation 2.2 (Nunes and Peinemann, 2001)

$$\alpha = \frac{\alpha_c(\frac{1}{P_{c1}}+\left(\frac{2}{P_{d1}}\right)-2\Phi(\frac{1}{P_{d1}}-\frac{1}{P_{c1}})(\frac{\alpha_c}{P_{c1}}+\frac{2}{P_{d2}}+\Phi\left(\frac{1}{P_{d2}}-\frac{\alpha_c}{P_{c1}}\right))}{(\frac{1}{P_{c1}}+\left(\frac{2}{P_{d1}}\right)+\Phi(\frac{1}{P_{d1}}-\frac{1}{P_{c1}})(\frac{\alpha_c}{P_{c1}}+\frac{2}{P_{d2}}-2\Phi\left(\frac{1}{P_{d2}}-\frac{\alpha_c}{P_{c1}}\right))} \qquad (2.2)$$

`Where α is the overall selectivity, and α_c is the selectivity of the continuous polymer phase. The indices 1 and 2 are referring to gas 1 and 2. At low loadings of dispersed zeolite, individual particle can be considered to be well separated. At higher loadings rate, some small islands of interconnected particles form and at even higher loadings, these islands will grow and connect to form extended pathways. Continuous channel will form within membranes and all zeolite particles are connected to the channels. This is called the percolation threshold and this threshold can only be achieved at particle loadings of about 30% The highly permeable zeolite only has a large effect on polymer permeability when the percolation threshold is reached (Baker, 2000).

However, according to Ismail, the permeability and selectivity of mixed matrix membrane can be calculated using formula for normal plain polymeric membrane. The permeability can be calculated by using equation 2.3.

$$P = \frac{Q}{A \times \Delta P} \qquad (2.3)$$

Where P is the permeability of the membrane, Q is the flowrate of gas species in, A is the area of the membrane and ΔP is the pressure difference across the membrane. The unit for permeability is in GPU and it can be calculated by using equation 2.4 (Norida, 2004).

$$1\ \text{GPU} = 1 \times 10^{-6} \frac{cm^3}{cmHg\ \ s\ cm^2} \qquad (2.4)$$

For the selectivity, α, of the membrane of species A from species B, it can be calculated by using this equation 2.5

$$\alpha = \frac{P_A}{P_B} \qquad (2.5)$$

To properly choose the dispersed and continuous phases, one must take the transport mechanisms and the gas component preferentially transporting through the membrane into consideration. In some cases, it is more sensible to allow the smaller component to pass through; therefore, inorganic fillers with molecular sieving characteristics and polymers based on the size selection should be combined to produce MMMs. On the other hand, the selective transport of more condensable molecules through the membrane is more economical in some industrial applications. To fulfil this target, the MMMs may include microporous media that favour a selective surface flow mechanism and polymers that separate the mixtures by solubility selectivity (Anand *et. al*, 1997; Rao and Sircar, 1996).

2.4 Zeolite and Surface Modification

2.4.1 Zeolite

Molecular sieve zeolites of the most important aluminosilicates can be represented by the chemical formula $M_{2/n}O.Al_2O_3.{}_ySiO_2.{}_wH_2O$ where *y* is 2 or greater, M is the charge balancing cation, such as sodium, potassium, magnesium and calcium, *n* is the cation valence, and *w* represents the moles of water contained in the zeolitic voids (Wan Aizan *et. al*, 2006).

Zeolite framework is made up of SiO_4 tetrahedral linked together by sharing of oxygen ions. The example of this kind of structure can be seen in Figure 2.3. This structure makes up channels and interconnected voids and this allows water molecules to occupy the space. (Wan Aizan *et. al*, 2006) Therefore we need to dry zeolite when we want to use it in order to remove water. The example of zeolite and its water sorption properties are shown in Table 2.3.

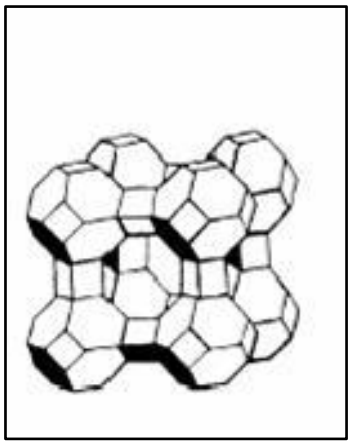

Figure 2.3: The tetrahedral molecular structure of zeolite 4A (Wan Aizan *et. al*, 2006)